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## (54) PRODUCTION OF EXHAUST GAS CLEANING CATALYST AND OBTAINED CATALYST

(57)Abstract:

PROBLEM TO BE SOLVED: To prevent the lowering of exhaust gas cleaning efficiency, especially, the lowering of NOx occluding quantity by using a single metal or composite metal colloid to which a catalytic metal is bonded by a chelating agent to support the same on a particulate porous carrier and further supporting an element such as an alkali metal or the like, on the carrier.

SOLUTION: Single metal or composite metal colloid to which a catalytic element is bonded by a chelating agent is prepared. That is, the chelating agent and a catalytic metal compd. are dissolved in and mixed with water and alcohol is added to the formed aq. soln. The resulting soln. is refluxed and filtered to be concn. until a target concn. is obtained. Next, the obtained single metal or composite metal colloid is supported on a porous carrier by a method wherein the carrier and the obtained metal colloid are stirred in the aq. soln. to adsorb and support the metal colloid on the carrier. Next, the supporting treatment of an element such as an alkali metal, or the like, is performed by adding a compound containing the element such as the alkali metal, or the like, to the aq. soln. after the supporting treatment of the single metal or composite metal colloid is completed.

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**CLAIMS**

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**[Claim(s)]**

[Claim 1]Either of the composite metal colloid produced by making carry out the chelate bond of single metal colloid or two or more sorts of catalyst metal produced by carrying out the chelate bond of one sort of metal by a chelating agent is used, Support a single metal or a composite metal to a porous body which is a fine grain, and An alkaline metal, A support method of a polymers chelate metal catalyst supporting one sort of an element belonging to either an alkaline metal, alkaline-earth metals and rare earth, or two sorts or more using solution containing one sort of a compound of an element belonging to either alkaline-earth metals and rare earth, or two sorts or more.

[Claim 2]It processes in solution containing one sort of a compound of an element which belongs a porous body which is a fine grain to either an alkaline metal, alkaline-earth metals and rare earth, or two sorts or more, Support one sort of an element belonging to either an alkaline metal, alkaline-earth metals and rare earth, or two sorts or more, and by a chelating agent after that. A support method of a polymers chelate metal catalyst supporting a single metal or a composite metal using either of the composite metal colloid produced by making carry out the chelate bond of single metal colloid or two or more sorts of catalyst elements which are produced by carrying out the chelate bond of one sort of metal.

[Claim 3]Are the method of supporting a catalyst metallic component to a monolith which carried out the coat of the porous body which is a fine grain, and a monolith which carried out the coat of the porous body by a chelating agent. Composite metal colloid produced by making carry out the chelate bond of single metal colloid or two or more sorts of catalyst metal produced by carrying out the chelate bond of one sort of metal is used, Support a single metal or a composite metal to a porous body, and one sort or two sorts or more of solution of a compound of an element which belongs there at either an alkaline metal, alkaline-earth metals and rare earth is added, A support method to a monolith of a polymers chelate metal catalyst making one sort of an element belonging to either an alkaline metal, alkaline-earth metals and rare earth, or two sorts or more support.

[Claim 4]It is the method of supporting a catalyst metallic component to a monolith which carried out the coat of the porous body which is a fine grain, One sort or two sorts or more of

solution of a compound of an element which belongs a monolith which carried out the coat of the porous body to either an alkaline metal, alkaline-earth metals and rare earth is used, Support one sort of an element belonging to either an alkaline metal, alkaline-earth metals and rare earth, or two sorts or more, and there by a chelating agent. A support method to a monolith of a polymers chelate metal catalyst adding either of the composite metal colloid produced by making carry out the chelate bond of single metal colloid or two or more sorts of catalyst elements which are produced by carrying out the chelate bond of one sort of metal, and supporting a single metal or a composite metal.

[Claim 5]A chelating agent Polyacrylic acid, polyallylamine, polymethacrylic acid, Polyvinyl amine, poly(N,N-dicarboxymethyl) allylamine, Polyvinyl imidazole, polyvinyl PIIRAZORU, polyacrylamide, Polyvinyl METOKISAZORIDON, polyamide of ethylene-diamine-tetraacetic acid and ethylenediamine, Polyamide of an acid anhydride of 1,2-cyclohexanediamine tetraacetic acid, and 1,2-diaminocyclohexane, Polyamide of 1,2-cyclohexanediamine tetraacetic acid and 1,2-diaminocyclohexane, Polyamide of 1,2-cyclohexanediamine tetraacetic acid and ethylenediamine, A support method of the polymers chelate metal catalyst according to claim 1 or 2 being any one sort of a copolymer of vinyl acetate and methacrylic acid, and the copolymer of itaconic acid and methacrylic acid, or two sorts or more.

[Claim 6]A support method of the polymers chelate metal catalyst according to claim 1 to 5, wherein catalyst metal to chelate is any one sort of platinum, rhodium, iridium, a ruthenium, palladium, silver, gold, osmium, and the rhenium, or two sorts or more.

[Claim 7]A support method of the polymers chelate metal-barium catalyst according to claim 1 to 6, wherein a porous body which is a fine grain is any one sort of alumina, silica, a silica alumina, zeolite, mordenite, a titania, Seria, and the zirconia, or two sorts or more.

[Claim 8]A barium compound used for support of barium among alkaline-earth metals, A support method of the polymers chelate metal catalyst according to claim 1 to 7 being any one sort of barium acetate, EDTA barium, CyDTA barium, barium nitrate, and barium tetranitroplatinate and barium chloroplatinate, or two sorts or more.

[Claim 9]A polymers chelate metal catalyst object acquired by the support method of the polymers chelate metal catalyst according to claim 1 to 6.

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[Translation done.]

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the catalyst acquired among the catalysts for exhaust gas purification by the catalyst metal support method of the catalyst for purification useful to especially the exhaust gas for cars, and the catalyst metal support method for the same.

[0002]

[Description of the Prior Art]The catalyst for exhaust gas purification, wherein the conventional catalyst for lean burn automobile exhaust purification consists of the barium oxide, the lanthanum oxide, and platinum which the carrier which is a porous body, and the carrier concerned were made to support so that JP,5-261287,A may see is known.

[0003]How to make this catalyst immersed the carrier which carried out the coat of the alumina to the mixed solution of the solution of a dinitrodiammine platinum nitric acid solution, barium acetate, or a barium nitrate, and lanthanum nitrate solution, calcinated after desiccation and was manufacturing.

[0004]

[Problem(s) to be Solved by the Invention]However, the conventional catalyst for lean burn automobile exhaust purification was weak to heat resistance, under continuous hot environments, sintering (condensation) of the platinum was carried out and the phenomenon in which an exhaust gas purifying rate, especially  $\text{NO}_x$  occlusion amount fell and carried out had generated it.

[0005>About sintering of this platinum, this artificer has advocated solving according to the catalyst which used polyvinyl-pyrrolidone (PVP is called.)-platinum / rhodium composite metal colloid.

[0006]However, when barium was supported for the catalyst using PVP-platinum / rhodium compound colloid and  $\text{NO}_x$  occlusion amount was investigated, it turned out that performance as prediction of the beginning [ occlusion amount /  $\text{NO}_x$  ] cannot be demonstrated.

[0007]As a result of examining in detail where this cause is, it became clear that, as for this

invention persons, there was a problem in the gestalt at the time of a catalyst being supported. That is, it came to obtain the conclusion that there is a problem in the dispersibility of barium at the time of supporting barium which is alkaline-earth metals to catalyst support.

[0008]

[Means for Solving the Problem]Then, by this invention persons' controlling sintering of platinum by using composite metal colloid, such as platinum-rhodium, and supporting barium to high distribution near the platinum, A catalyst acquired by a catalyst metal support method and a catalyst metal support method of a catalyst for emission gas purification for cars which raised the dispersibility of the following barium as what acquires a catalyst for emission gas purification for cars which has conventionally outstanding NO<sub>x</sub> occlusion ability was developed.

[0009]And if a catalyst metal support method concerning this invention is used, it will become possible not only composite metal colloid but to acquire a barium support type catalyst usable as an exhaust gas catalyst for cars, even if it is single metal colloid. A catalyst particle and a catalyst particle condense sintering here, and it means a coarse-grain-ized phenomenon. If a catalyst particle coarse-grain-izes, a fall of a catalytic reaction interfacial area of a catalyst particle and exhaust gas will be caused, and a result to which purification performance of exhaust gas is reduced will be brought.

[0010]Either of the composite metal colloid produced by making carry out the chelate bond of single metal colloid or two or more sorts of catalyst metal produced by carrying out the chelate bond of one sort of metal by a chelating agent to claim 1 is used, Support a single metal or a composite metal to a porous body which is a fine grain, and An alkaline metal, It was considered as a support method of a polymers chelate metal catalyst supporting one sort of an element belonging to either an alkaline metal, alkaline-earth metals and rare earth, or two sorts or more using solution containing one sort of a compound of an element belonging to either alkaline-earth metals and rare earth, or two sorts or more.

[0011]It processes in solution which contains in claim 2 one sort of a compound of an element which belongs a porous body which is a fine grain to either an alkaline metal, alkaline-earth metals and rare earth, or two sorts or more, Support one sort of an element belonging to either an alkaline metal, alkaline-earth metals and rare earth, or two sorts or more, and by a chelating agent after that. It is considered as a support method of a polymers chelate metal catalyst supporting a single metal or a composite metal using either of the composite metal colloid produced by making carry out the chelate bond of single metal colloid or two or more sorts of catalyst elements which are produced by carrying out the chelate bond of one sort of metal.

[0012]The biggest feature of these catalyst metal support methods is at a point of performing support of an element ("elements, such as an alkaline metal," is called.) belonging to either an alkaline metal, alkaline-earth metals and rare earth, and support with other catalyst elements as a separate process. A method according to claim 1 supports a single metal or a composite metal to a porous body which is a carrier first, and supports elements, such as an alkaline metal, after that to it. On the other hand, a method according to claim 2 differs in an order which supports elements, such as an alkaline metal, to a porous body which is a carrier first,

supports a single metal or composite metal colloid after that to it, and is supported.

[0013]Thus, even if it put in and changed an order of elements, such as an alkaline metal, and a single metal or a composite metal to support, it became clear that it was changeless for performance of a catalyst which is a final product in any way as a result of research. As compared with an effect of conventional technology which is what performs simultaneously support with elements, such as an alkaline metal, and a single metal or a composite metal, this. High decentralization of elements, such as an alkaline metal made into the purpose, is attained by not supporting elements, such as an alkaline metal, simultaneously with support of a single metal or a composite metal like this invention, but providing a step of support processing of elements, such as an alkaline metal, separately.

[0014]A reaction procedure divided into three steps has the invention according to claim 1. First step creates a single metal or composite metal colloid to which the chelate bond of the catalyst element was carried out by a chelating agent. That is, dissolution mixing of a chelating agent and the catalyst metallic compounds is carried out in solution, and alcohol, such as ethanol, is added, and after a predetermined time rotary flow, it filters and obtains by condensing until it becomes the target catalyst metal concentration.

[0015]It is desirable to use for a chelating agent here what was indicated to claim 5. Specifically Polyacrylic acid, polyallylamine, polymethacrylic acid, Polyvinyl amine, poly(N,N-dicarboxymethyl) allylamine, Polyvinyl imidazole, polyvinyl PIIRAZORU, polyacrylamide, Polyvinyl METOKISAZORIDON, polyamide of ethylene-diamine-tetraacetic acid and ethylenediamine, Polyamide of an acid anhydride of 1,2-cyclohexanediamine tetraacetic acid, and 1,2-diaminocyclohexane, Polyamide of 1,2-cyclohexanediamine tetraacetic acid and 1,2-diaminocyclohexane, Any one sort of polyamide of 1,2-cyclohexanediamine tetraacetic acid and ethylenediamine, a copolymer of vinyl acetate and methacrylic acid, and the copolymer of itaconic acid and methacrylic acid or two sorts or more are used.

[0016]These chelating agents are easy to remove by a baking process after excelling in the chelation effect and performing catalyst support, and it is very rare to affect catalyst performance. Rather than anything, the chelating agent hung up here can distribute a catalyst metallic particle over high distribution. Without particle diameter of a catalyst particle in the state where it supported varying in the range which are 1 - 100 nm of numbers, high distribution shall have the particle size distribution of about \*\*20% of mean particle diameter, and shall tell the above and the following that it is in the state where it distributed uniformly on the occasion of support.

[0017]The necessity for distributing a catalyst metallic particle over high distribution serves as conditions searched for when it is going to support elements, such as an alkaline metal supported as a separate process, to high distribution. That is, if chelated catalyst metal cannot be made to high-decentralize, support of elements, such as an alkaline metal performed after support of the catalyst metal concerned, cannot be high-decentralized, either. If elements, such as an alkaline metal, are not supported with a case where elements, such as an alkaline metal, are supported first by high distribution so that it may indicate to claim 2 mentioned later, it is considered that it cannot make chelated catalyst metal high-decentralize. By using a

chelating agent stated above, it becomes possible to make chelated catalyst metal high-decentralize.

[0018]And it seems that there is no restriction in particular in catalyst metal to chelate. In claim 6, an effect of application of this invention has indicated as a clearly remarkable thing at a place of this artificer's research. It can use for catalyst metal to chelate, combining selectively any one sort of platinum, rhodium, iridium, a ruthenium, palladium, silver, gold, osmium, and the rhenium, or two sorts or more.

[0019]When using combining two or more sorts selectively, particles of at least one sort of catalyst metal cover the circumference of other metallic colloid particles, become what plays a role of protective colloid, and can maintain high catalyst performance over a long period of time. For example, if it is the combination of platinum and rhodium, rhodium colloid will cover the surface of platinum colloid and a role which protects platinum colloid will be played.

[0020]Some compounds used as a supply source of above-mentioned catalyst metal are various. In the case of single catalyst metallic colloid, it is sufficient if it is used [ for the purpose of a compound containing one sort of catalyst metal / suitably ] selectively. However, for example, many kinds of optimal combination exists as it is preferred as a platinum compound to use dinitrodiammine platinum and it is preferred to use nitric acid rhodium as a rhodium compound, in order to obtain platinum-rhodium composite metal colloid.

[0021]Optimal combination should be defined in consideration of the various characteristics of whether on the occasion of actual use, high catalyst performance is securable in the ability to support [ whether it excels in the long-term stability of quality of colloid, and ] easily. Anyway, in consideration of affinity with a chelating agent to be used, a suitable compound containing above-mentioned catalyst metal can be used selectively suitably.

[0022]As the second step, single metal colloid or composite metal colloid obtained by first step is supported to a porous body used as a carrier. Alumina, silica, a silica alumina, zeolite, mordenite, a titania, Seria, and zirconia which were indicated to claim 7 can be used for a porous body here. It is useful to use alumina, if an economical field is taken into consideration, and alternative use doubled with the purpose of using a final catalyst, such as using mordenite with width of selection if there is the necessity of taking a diameter of porosity into consideration, is possible.

[0023]A support method carries out predetermined time churning of a carrier of the specified quantity, and the metallic colloid obtained by first step in solution, and is performed by carrying out adsorption support. At this time, desiccation of 110 °C x 2 hours may be performed for the purpose of more positive support of catalyst metal, and baking treatment of 450 °C x 2 hours may be performed if needed. And support processing of elements, such as an alkaline metal, is performed as the third step.

[0024]Support processing of predetermined time of the second step is completed, and support of elements, such as an alkaline metal of the third step, is performed by adding a compound which contains elements, such as an alkaline metal, in the solution. If it adds as solution form and agitates, a compound which contains elements, such as an alkaline metal, at this time does not have maldistribution in a solution, and can be distributed uniformly.

[0025]Since especially barium is used for an exhaust gas cleaning catalyst of a car and it is used for adsorption treatment of  $\text{NO}_x$  also in elements, such as an alkaline metal, it is a very important element. Barium compounds suitable for using for support of this barium are barium acetate, EDTA barium, CyDTA barium, barium nitrate, and barium tetranitroplatinate and barium chloroplatinate, as indicated to claim 8. If these barium compounds are used in a support method concerning this invention, it will become possible to make it support as particles of barium with a high degree of dispersion distributed minutely and uniformly.

[0026]Then, moisture is made to evaporate to dryness, a drying process is performed, it calcinates with prescribed temperature for several hours, and manufacture of the polymers chelate metal catalyst object according to claim 7 is completed. This polymers chelate metal catalyst has the high dispersibility of other catalyst metal, such as an alkaline metal, advance of sintering of catalyst metal is stopped, and it becomes possible to maintain  $\text{NO}_x$  occlusion ability which does not have degradation of catalyst performance and was excellent also in the bottom of hot environments.

[0027]Unlike claim 1, the invention according to claim 2 supports elements, such as an alkaline metal, first. Support of elements, such as an alkaline metal performed first, adds a porous body which is a carrier in solution which dissolved a compound which contains elements, such as same alkaline metal, with having used at the third step described by explanation of a catalyst metal support method of above-mentioned claim 1, By carrying out predetermined time churning, there is no maldistribution and distributed support is carried out uniformly. At this time, desiccation of 110 °C x 2 hours may be performed for the purpose of more positive support of an alkaline metal etc., and baking treatment of 600 °C x 2 hours may be performed if needed.

[0028]Next, although single metal colloid or composite metal colloid is made, since it is the same in explanation of first step of claim 1 having shown about this, a duplicate statement is omitted.

[0029]Then, in solution which dissolved elements, such as an alkaline metal, this single metal colloid or composite metal colloid is added into a solution which support of elements, such as an alkaline metal, completed, and also predetermined time churning is continued, and support processing of a single metal or a composite metal is performed.

[0030]Eventually, moisture is made to evaporate to dryness, a drying process is performed like the invention according to claim 1, it calcinates with prescribed temperature for several hours, and manufacture of the polymers chelate metal catalyst object according to claim 9 is completed.

[0031]If this polymers chelate catalyst is used as an exhaust gas purifying catalyst of a car as especially mentioned above, stable occlusion of  $\text{NO}_x$  which was not able to be obtained with the conventional catalyst will become possible, and it will become realizable [ an outstanding LEV car ].

[0032]A support method of a catalyst described above is the method of supporting a catalyst directly to a porous body which is a fine grain, i.e., a granular material. Below, the coat of the



surface of a monolith which is a component of a catalyst body is carried out by a porous body which is a fine grain beforehand, and a support method to a monolith of a polymers chelate metal catalyst which supports catalyst metal to a porous body is explained after that. Material used for manufacture of winding-up catalysts, such as metal waveform foil and metal spacer foil, and a square-shaped lamination catalyst with a monolith at the above and the following, It uses as a concept containing all the members that constitute catalyst bodies, such as a component of a ceramic honeycomb, and a ceramic honeycomb which carried out integral moulding.

[0033]An object of an invention explained below is to improve the adsorptivity of catalyst metal in catalyst metal support at the time of supporting catalyst metal. When supporting catalyst metal, using PVP as catalyst metallic colloid, generally it is difficult to once support compared with supporting directly to a porous body which is a fine grain to a porous body which is the fine grain which carried out the coat to a monolith. When starting, an adsorption rate at the time of making catalyst metal adsorb gets remarkably bad.

[0034]Using a monolith which carried out the coat of the porous body which is a fine grain as a means to solve this problem by performing separately support of elements, such as an alkaline metal, and support of other metal catalyst elements, An adsorption rate can be raised and the state where elements, such as an alkaline metal, distributed minutely uniformly can be acquired. There are not the manufacturing method according to claim 1 or 2 fundamentally supported directly to a porous body which is a fine grain, and a place which changes in any way. And stable outstanding adsorption performance is securable by choosing a high polymer chelating agent properly.

[0035]Are the method of supporting a catalyst metallic component to a monolith which carried out the coat of the porous body which is a fine grain to claim 3, and a monolith which carried out the coat of the porous body by a chelating agent. Composite metal colloid produced by making carry out the chelate bond of single metal colloid or two or more sorts of catalyst metal produced by carrying out the chelate bond of one sort of metal is used, Support a single metal or a composite metal to a porous body, and one sort or two sorts or more of solution of a compound of an element which belongs there at either an alkaline metal, alkaline-earth metals and rare earth is added, It is considered as a support method to a monolith of a polymers chelate metal catalyst making one sort of an element belonging to either an alkaline metal, alkaline-earth metals and rare earth, or two sorts or more support.

[0036]First a support method according to claim 3 to a porous body which is the fine grain which carried out the coat to a monolith by a chelating agent. It is the support method which supports either of the composite metal colloid produced by making carry out the chelate bond of single metal colloid or two or more sorts of catalyst metal produced by carrying out the chelate bond of one sort of metal, and supports elements, such as an alkaline metal, continuously.

[0037]Here, a porous body which is a fine grain is one sort of alumina indicated to claim 7, silica, a silica alumina, zeolite, mordenite, a titania, Seria, and zirconia, or two sorts or more. A coat to a monolith of this porous body immerses a monolith into solution which made a porous

body suspended, and a porous body of a multiple-times repetition and the amount of the purposes carries out the coat of the process to dry.

[0038]Each compound according to claim 5 can be used for a chelating agent as mentioned above. About a reason to which it was presupposed that these compounds are used, since it becomes the statement which is the same as that of the above-mentioned, and overlapped, it omits.

[0039]With catalyst metal used for composite metal colloid produced by making carry out the chelate bond of single metal colloid or two or more sorts of catalyst metal produced by carrying out the chelate bond of one sort of metal by a chelating agent. It is preferred to use combining selectively any one sort of platinum indicated to claim 6, rhodium, iridium, a ruthenium, palladium, silver, gold, osmium, and the rhenium or two sorts or more. About how to combine, it is the same as that of the above-mentioned, and duplicate explanation is omitted.

[0040]Among compounds containing elements, such as an alkaline metal, it is preferred also about a barium compound to use the barium compound according to claim 8, and it is the same as that of the above-mentioned also about a reason for having adopted these.

[0041]It is the method of supporting a catalyst metallic component to a monolith which carried out the coat of the porous body which is a fine grain to claim 4, One sort or two sorts or more of solution of a compound of an element which belongs a monolith which carried out the coat of the porous body to either an alkaline metal, alkaline-earth metals and rare earth is used, Support one sort of an element belonging to either an alkaline metal, alkaline-earth metals and rare earth, or two sorts or more, and there by a chelating agent. It is considered as a support method to a monolith of a polymers chelate metal catalyst adding either of the composite metal colloid produced by making carry out the chelate bond of single metal colloid or two or more sorts of catalyst elements which are produced by carrying out the chelate bond of one sort of metal, and supporting a single metal or a composite metal.

[0042]First, support, and this support method according to claim 4 continuously elements, such as an alkaline metal, to a porous body which is the fine grain which carried out the coat to a monolith by a chelating agent. It is the support method which supports either of the composite metal colloid produced by making carry out the chelate bond of single metal colloid or two or more sorts of catalyst metal produced by carrying out the chelate bond of one sort of metal.

[0043]Here by coat method to a monolith of a porous body and a porous body which is a fine grain, chelating agent, and a chelating agent. About a compound containing elements used for composite metal colloid produced by making carry out the chelate bond of single metal colloid or two or more sorts of catalyst metal produced by carrying out the chelate bond of one sort of metal, such as catalyst metal and an alkaline metal. Since there are not the invention according to claim 3 and a place which changes in any way, a statement about the contents is omitted.

[0044]By support in the state where a degree of dispersion of barium is high being possible, and using each compound according to claim 5 as a chelating agent further, if a support method of the above catalyst metal according to claim 3 or 4 is adopted. Even if it is a porous body in the state where the coat was carried out to a monolith, an adsorption rate to a porous

body of a chelated catalyst element can be carried out more early. As a result, adsorption time can be shortened and it can contribute to a productivity drive of a product.

[0045]In order to explain more nearly plainly claim 3 and the effect of the invention according to claim 4, When a honeycomb which carried out the coat of the alumina to platinum colloid which is the single catalyst metallic colloid which used polyacrylic acid (PAA is called hereafter.) for a chelating agent concerning this invention is immersed, Adsorption support speed of platinum which is catalyst metal with a case where a polyvinyl pyrrolidone (PVP is called hereafter.) is used is measured. A relation of platinum concentration and adsorption (support) time which remained in platinum colloid is shown in drawing 1. Remains platinum concentration in a solution at this time measured and asked for a solution in ion plasma emission spectrochemical analysis.

[0046]As for it, according to this drawing 1, compared with a case where PVP is used, a thing using PAA as a chelating agent turns out that the amount of remains platinum is decreasing quickly temporally, and platinum which is a catalyst element becomes very quick compared with a case where PVP is used in speed which carries out adsorption support. If adsorptivity and stability are taken into consideration, the range of weight ratio (M/P) =1 of catalyst metal (M) and a chelating agent (P) / 4 - 1/0.2 will serve as the best adsorption rate. Also in this range, the range of weight ratio (M/P) =1 / 3 - 1/1 shows an adsorption rate quick in peak. And not only an adsorption rate but outstanding dispersibility can be attained.

[0047]Thus, it becomes possible to also raise the dispersibility of elements, such as an alkaline metal collectively supported from the dispersibility of catalyst metal, such as platinum, being improved.

[0048]

[Embodiment of the Invention]Hereafter, the embodiment considered to be best [ about this invention ] is described.

[0049]A 1st embodiment: Dissolution mixing of the polyacrylic acid 2g of 8.688 g of dinitrodiammine platinum (platinum concentration 4.604%) and the molecular weight 2000 was carried out first at 450 ml of water, 112.5 ml of ethanol was added, and it returned for 5 hours. Suction filtration of this was carried out, it was condensed, and it adjusted as polyacrylic acid-platinum colloid of 0.5623-% of the weight platinum.

[0050]Next, the alumina 4g used as a carrier was added into 40 ml of polyacrylic acid-platinum colloid of the above-mentioned 0.5623-% of the weight platinum, and was agitated for 30 minutes, and platinum support was performed. The barium acetate 3.40g was added, it agitated for 16 hours, and barium was combined.

[0051]When combination of barium was completed, it evaporated to dryness, and calcinated on the conditions of 600 °C x 2 hours after desiccation of 110 °C x 2 hours, and the catalyst was adjusted. It became a catalyst with result, platinum 2g, and barium 0.2mol and the presentation of 120 g of alumina (aluminum<sub>2</sub>O<sub>3</sub>).

[0052]Gas occlusion is made to perform until it makes the mixed gas which contained NO<sub>x</sub> using this catalyst contact and is saturated, The occlusion of NO<sub>x</sub> and the check of discharge

were performed by measuring the wave number of the  $\text{NO}_3^-$  peak of FT-IR, and the occlusion amount measured the amount of discharge  $\text{NO}_x$  in TG-DTA, and made it the  $\text{NO}_x$  occlusion amount. This method is the same as that of the following. They were the  $\text{NO}_x$  occlusion amount 24.7 (mg/g) at this time, and 19.9% of a barium capacity factor. The mixed gas said here has the presentation of NO 1000ppm,  $\text{O}_2$  5%, and  $\text{N}_2$  balance. A barium capacity factor is a thing [ as opposed to / a thing / a theoretical occlusion amount ] of the rate of a survey occlusion amount.

[0053]A 2nd embodiment: Dissolution mixing of the polyacrylic acid 2g of 8.688 g of dinitrodiammine platinum (platinum concentration 4.604%) and the molecular weight 2000 was carried out first at 450 ml of water, 112.5 ml of ethanol was added, and it returned for 5 hours. Suction filtration of this was carried out, it was condensed, and it adjusted as polyacrylic acid-platinum colloid of 0.5623-% of the weight platinum.

[0054]Next, the alumina 4g used as a carrier was added into 40 ml of polyacrylic acid-platinum colloid of the above-mentioned 0.5623-% of the weight platinum, and was agitated for 30 minutes, and platinum support was performed. The potassium nitrate 0.97g was added, it agitated for 16 hours, and potassium was combined.

[0055]When combination of potassium was completed, it evaporated to dryness, and calcinated on the conditions of 600 °C x 2 hours after desiccation of 110 °C x 2 hours, and the catalyst was adjusted. It became a catalyst with result, platinum 2g, and potassium 0.2mol and the presentation of 120 g of alumina ( $\text{aluminum}_2\text{O}_3$ ).

[0056]Gas occlusion is made to perform until it makes the mixed gas which contained  $\text{NO}_x$  using this catalyst contact and is saturated, The occlusion of  $\text{NO}_x$  and the check of discharge were performed by measuring the wave number of the  $\text{NO}_3^-$  peak of FT-IR, and the occlusion amount measured the amount of discharge  $\text{NO}_x$  in TG-DTA, and made it the  $\text{NO}_x$  occlusion amount. This method is the same as that of the following. They were  $\text{NO}_x$  occlusion amount 25.3 mg/g at this time, and 20.0% of a potassium capacity factor. The mixed gas said here has the presentation of NO 1000ppm,  $\text{O}_2$  5%, and  $\text{N}_2$  balance. A barium capacity factor is a thing [ as opposed to / a thing / a theoretical occlusion amount ] of the rate of a survey occlusion amount.

[0057]A 3rd embodiment: First 41.2844 g of dinitrodiammine platinum (platinum concentration 4.578%), Dissolution mixing of 1.108 g of nitric acid rhodium (10.00% of rhodium concentration) and the polyacrylic acid 8g of the molecular weight 32400 was carried out at 2000 ml of water, 500 ml of ethanol was added, and it returned for 7 hours. This was condensed by suction filtration and it adjusted as the polyacrylic acid-platinum / rhodium composite metal colloid of 1.195-% of the weight platinum and 0.069-% of the weight rhodium.

[0058]Next, the polyacrylic acid-platinum / rhodium composite metal colloid 16.74g of the alumina 12g used as a carrier, and the above-mentioned 1.195-% of the weight platinum and

0.069-% of the weight rhodium were added into 80 ml of water, it agitated for 30 minutes, and platinum-rhodium support was performed. The solution in which 40 ml of water was made to dissolve the barium acetate 5.11g was added, it agitated for 16 hours, and barium was combined.

[0059]When combination of barium was completed, it evaporated to dryness with the rotary evaporator, and calcinated on the conditions of 600 °C x 2 hours after desiccation of 110 °C x 2 hours, and the catalyst was adjusted. a result -- the platinum 1.8g and rhodium -- it became a catalyst with 0.2 g, barium 0.2mol, and the presentation of 120 g of alumina (aluminum<sub>2</sub>O<sub>3</sub>).

[0060]When the mixed gas which contained NO<sub>x</sub> using this catalyst is made to contact and NO<sub>x</sub> occlusion was made to perform, they were the NO<sub>x</sub> occlusion amount 30.2 (mg/g) and 24.4% of a barium capacity factor. The statement which overlapped since it was the same as a first embodiment is abbreviated to the mixed gas and the barium capacity factor which are said here.

[0061]A 4th embodiment: First 41.2844 g of dinitrodiammine platinum (platinum concentration 4.578%), Dissolution mixing of 1.108 g of nitric acid rhodium (10.00% of rhodium concentration) and 8 g of the polyallylamine of the molecular weight 50000 was carried out at 2000 ml of water, 500 ml of ethanol was added, and it returned for 7 hours. Suction filtration of this was carried out, it was condensed, and it adjusted as the polyallylamine platinum / rhodium composite metal colloid of 1.195-% of the weight platinum and 0.069-% of the weight rhodium.

[0062]Next, the solution which made 40 ml of water dissolve the EDTA barium 6g in the alumina 12g used as a carrier was added, and after carrying out churning adsorption for 1 hour, it evaporated to dryness, dried on the conditions of 110 °C x 2 hours, and calcinated on the conditions of 600 °C x 2 hours. The polyallylamine platinum / rhodium colloid 16.74g of the above-mentioned 1.195-% of the weight platinum and 0.069-% of the weight rhodium were added into 80 ml of water at this, it agitated for 30 minutes, and platinum-rhodium support was performed.

[0063]When support was completed, it evaporated to dryness with the rotary evaporator, and calcinated on the conditions of 450 °C x 2 hours after desiccation of 110 °C x 2 hours, and the catalyst was adjusted. a result -- the platinum 1.8g and rhodium -- it became a catalyst with 0.2 g, barium 0.2mol, and the presentation of 120 g of alumina (aluminum<sub>2</sub>O<sub>3</sub>).

[0064]When the mixed gas which contained NO<sub>x</sub> using this catalyst is made to contact and NO<sub>x</sub> occlusion was made to perform, they were the NO<sub>x</sub> occlusion amount 30.0 (mg/g) and 25.0% of a barium capacity factor. The statement which overlapped since it was the same as a first embodiment is abbreviated to the mixed gas and the barium capacity factor which are said here.

[0065]A 5th embodiment: It was immersed into the solution which made alumina suspended, and was made to dry at 110 °C for 2 hours, and the waveform metal foil 50 micrometers in thickness, 5 cm in width, and 25 cm in length and spacer foil which were able to be first done

with the stainless steel which is a monolith were calcinated at 600 °C for 2 hours. As a result, the coat was carried out to the surface of waveform metal foil and spacer foil with alumina of 2 g of totals. The waveform metal foil and spacer foil which carried out the coat with this alumina were wound up in piles, and the catalyst body was formed.

[0066]And 41.2844 g of dinitrodiammine platinum (platinum concentration 4.578%), Dissolution mixing of 1.108 g of nitric acid rhodium (10.00% of rhodium concentration) and 8 g of the polyallylamine of the molecular weight 50000 was carried out at 2000 ml of water, 500 ml of ethanol was added, and it returned for 7 hours. Suction filtration of this was carried out, it was condensed, and it adjusted as the polyallylamine platinum / rhodium composite metal colloid of 1.195-% of the weight platinum and 0.069-% of the weight rhodium.

[0067]Next, the catalyst body (honeycomb) which wound up in piles the waveform metal foil which carried out the coat with this alumina, and spacer foil was immersed for 4 hours into the solution which diluted above-mentioned polyallylamine platinum / rhodium composite metal colloid until it became the platinum concentration of 350 ppm. When support was completed, it evaporated to dryness and calcinated on the conditions of 450 °C x 2 hours after desiccation of 110 °C x 2 hours. While being immersed in the colloidal solution, churning is continued and the maldistribution of catalyst metal was kept from taking place a solution.

[0068]Then, the honeycomb was put in the solution made to dissolve the EDTA barium 6g in 40 ml of water, after carrying out churning adsorption for 1 hour, it evaporated to dryness, dried on the conditions of 110 °C x 2 hours, and calcinated on the conditions of 600 °C x 2 hours, and barium was supported.

[0069]When the mixed gas which contained  $\text{NO}_x$  using this catalyst is made to contact and  $\text{NO}_x$  occlusion was made to perform, they were  $\text{NO}_x$  occlusion amount 30.2 mg/g and 25.2% of a barium capacity factor. The statement which overlapped since it was the same as a first embodiment is abbreviated to the mixed gas and the barium capacity factor which are said here.

[0070]Comparison sample 1: Here, as a comparison sample with a 1st above-mentioned embodiment and a 2nd embodiment, dissolution mixing of 8.688 g of the dinitrodiammine platinum (platinum concentration 4.604%) was carried out at 450 ml of water, the alumina 12.0g used as a carrier was added, it agitated for 30 minutes and adsorption support was carried out. And this was separated and rinsed, it calcinated on the conditions of 450 °C x 2 hours after desiccation of 110 °C x 2 hours, and the platinum-alumina catalyst was adjusted.

[0071]Next, what dissolved 1.7g barium acetate in 20 ml of water was added to 9.15 g of this platinum-alumina catalyst, it agitated to it for 16 hours, and barium was combined with it.

[0072]When combination of barium was completed, it evaporated to dryness with the rotary evaporator, and calcinated on the conditions of 600 °C x 2 hours after desiccation of 110 °C x 2 hours, and the catalyst was adjusted. The catalyst with result, platinum 2g, and barium 0.2mol and the presentation of 120 g of alumina ( $\text{aluminum}_2\text{O}_3$ ) was acquired. This was made into the comparison sample 1.

[0073]When the mixed gas which contained  $\text{NO}_x$  using this comparison sample 1 is made to

contact and  $\text{NO}_x$  occlusion was made to perform, they were the  $\text{NO}_x$  occlusion amount 18.5 (mg/g) and 14.9% of a barium capacity factor. The statement which overlapped since it was the same as a first embodiment is abbreviated to the mixed gas said here. The comparison result using this comparison sample 1 is indicated to Table 1.

[0074]

[Table 1]

| 使用触媒   | $\text{NO}_x$ 吸蔵量 (mg/g) | バリウム等利用率 (%) |
|--------|--------------------------|--------------|
| 第1実施形態 | 24.7                     | 21.6         |
| 第2実施形態 | 25.3                     | 20.0         |
| 比較試料1  | 18.5                     | 14.9         |

[0075]Comparison sample 2: As a comparison sample after a 3rd embodiment, further 41.2844 g of dinitrodiammine platinum (platinum concentration 4.578%), and 1.108 g of nitric acid rhodium (10.00% of rhodium concentration), Dissolution mixing of 8 g of the polyvinyl pyrrolidones of the molecular weight 25000 was carried out, the alumina 12g which is a carrier was added, and it agitated for 30 minutes, and calcinated after adsorption support for 450 °C x 2 hours.

[0076]The barium acetate 5.11g was added after calcination, it agitated for 16 hours, and barium was combined. When combination of barium was completed, it evaporated to dryness with the rotary evaporator, and calcinated on the conditions of 600 °C x 2 hours after desiccation of 110 °C x 2 hours, and the catalyst was adjusted. a result -- the platinum 1.8g and rhodium -- the catalyst with 0.2 g, barium 0.2mol, and the presentation of 120 g of alumina ( $\text{aluminum}_2\text{O}_3$ ) was acquired. This was made into the comparison sample 2.

[0077]When the mixed gas which contained  $\text{NO}_x$  using this comparison sample 2 is made to contact and  $\text{NO}_x$  occlusion was made to perform, they were  $\text{NO}_x$  occlusion amount of 27.7mg/g, and 22.4% of a barium capacity factor. The statement which overlapped since it was the same as a first embodiment is abbreviated to the mixed gas and the barium capacity factor which are said here.

[0078]To Table 1, the performance of the catalyst acquired by an above embodiment and the performance of the catalyst made into the comparison sample were compared and published.

[0079]

[Table 2]

| 使用触媒   | $\text{NO}_x$ 吸蔵量 (mg/g) | バリウム利用率 (%) |
|--------|--------------------------|-------------|
| 第3実施形態 | 30.2                     | 24.4        |
| 第4実施形態 | 30.0                     | 25.0        |
| 第5実施形態 | 30.2                     | 25.2        |
| 比較試料2  | 27.7                     | 22.4        |

[0080]As shown in Table 1 and 2, when the comparison sample 1 and the comparison sample 2 are contrasted with the embodiment which can be compared, respectively,  $\text{NO}_x$  occlusion

amount and the barium capacity factor of the catalyst which are applied to the embodiment of this invention in any case serve as a dramatically outstanding value.

[0081]

[Effect of the Invention]The polymers chelate metal-barium catalyst concerning this invention becomes the degree of dispersion of barium is high and possible [ maintaining the outstanding catalyst performance ]. If this polymers chelate metal-barium catalyst is used as an exhaust gas purifying catalyst of a car, compared with the conventional catalyst, the stable occlusion of  $\text{NO}_x$  will become possible and it will become realizable [ the LEV car using an internal-combustion engine ].

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[Translation done.]



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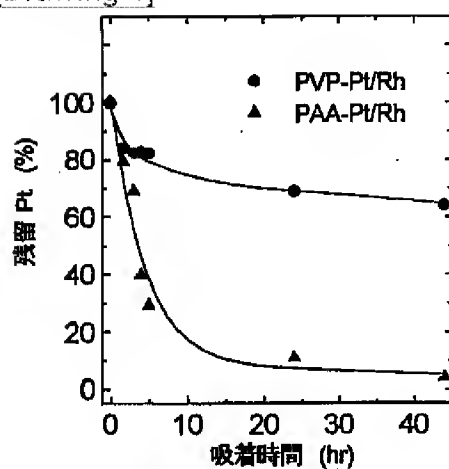
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DRAWINGS

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[Drawing 1]



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[Translation done.]